PRELIMINARY ECOMOMIC EVALUATION OF THE TREATMENT OF CANMET RESIDUE BY HYDROGEN PLASMA

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by

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April 5, 1991

Dr. Michio Ikura
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Dear Michio:

Further to my preliminary economic analysis of the plasma process for the treatment of CANMET residue, I have managed to obtain a range of market prices for acetylene. My contact was M. Dejardins of Linde in Montreal. He quoted a price varying from $\$5.00/m^3$ to $\$14.00/m^3$ depending on the rate of consumption. This works out to \$4.57-12.80/kg. I am sure that this price is high because the gas comes in bottles but it does make the production cost of \$0.35/kg seem very reasonable.

I have just sent the final report and the economic assessement to I.R. McGill and you should shortly be receiving 10 copies of each as per the contract.

Best regards

Sincerely yours

R.J. Munz
Associate Professor and Associate Director
Plasma Technology Research Centre (CRTP)

PRELIMINARY ECONOMIC EVALUATION OF THE TREATMENT OF CANMET RESIDUE BY HYDROGEN PLASMA

SUMMARY

A preliminary estimate has been made of the capital and operating cost of a plasma process for the hydrogen treatment of 10 000 kg/h of CANMET coprocessing residue. The products would be aceyelene and ash. The capital cost of the plant is $50M (Canadian 1986) while the operating cost is $22M (Canadian 1986). This operating cost is about $0.35/kg acetylene. It must be recalled that an important by-product of the process is the treatment of the CANMET waste.

INTRODUCTION

In this report we provide a estimate of the capital and operating cost of treating CANMET residue from a 100 000 barrel a day coprocessing plant using a hydrogen plasma. It is assumed that 10 000 kg/h of the residue must be processed. The economic assessment is heavily based on the report entitled "Technical and economic assessment of producing liquid fuels from natural gas via an electricity-based acetylene process, Phase II" by Cooke et al of SNC in 1986. The process described in that report used natural gas as the source of carbon for the production of gasoline using plasma produced acetylene as an intermediate. The acetylene was then hydrogenated to gasoline using a Mobil catalytic process.

The plant described in the above report was to produce 12 500 barrels per day (1 987 000 litres/day) of gasoline giving an acetylene production of 61 384 kg/h of acetylene. The plant described in the present work would have an acetylene capacity of about 13% of that in the SNC report. The original report examined three different quench chemicals; we have chosen to examine only the case of using hydrogen as the quench medium since this most closely reflects the residue treatment process. Only cost figures for the part of the plant which produce and purify the acetylene have been retained for the study. The factored costs for such things as land and buildings have been prorated on the basis of capital cost.

The production of acetylene from hydrocarbon sources using plasma technology requires modular reactors about 9 MW in electrical capacity and thus the present plant would require about 8 reactors. This report may be considered an optimistic evaluation since thermodynamically possible and complete conversions are assumed in the absence of experimental data at this point. The specific energy consumption figures of the SNC report are used directly although it is clear that the treatment of such a material as the CANMET residue will be more difficult than the treatment of a clean raw material such as natural gas.

An examination of the composition of the residue indicates that it contains sufficient

hydrogen to convert all carbon, which will not form CO, to acetylene. Thus, although some hydrogen will have to be recycled as the quench and plasma gas, no new hydrogen will have to be purchased. Very little if any hydrogen will be available as a by-product.

PROCESSING STEPS

The main processing steps are :

1. Acetylene Reactor/Quenching (Huels type reactor and hydrogen quench)

2. Gas purification and primary production separation (includes dry carbon separation in cyclones, water scrubbers for wet carbon, oil scrubbers for any naphthalenes and methanol scrubbers for higher acetylene removal)

CAPITAL COST

A capital cost summary of the plant is given below in Table 1. This is in January 1986 $ Canadian which are the units used in the SNC report. Only the parts of the plant relating to the production of acetylene and the cleaning of the product gases are included. The cost data of the SNC report were considered accurate to within about 20%. No adjustments have been made for differences in the feeding system for residue rather than natural gas or in the purification of the reaction products. It is expected that both of these aspects would add somewhat to the capital cost of the present plant. The total capital investment is about $50M (1986).

OPERATING COST

The estimated operating costs of the proposed process are summarized in Table 2 below, again in 1986 Canadian dollars. The treatment is almost identical to the SNC report. The major changes are that the product is acetylene, no raw materials are needed, and no by-products can be sold. The projected cost for acetylene is $ 0.35/kg. The original SNC estimate and this work both assume a cost of electricity of $.02/kWh. The present cost is likely to be higher.

REFERENCES

Cooke, N.E., F.A. Ashraf et al, "Conceptual design and techno-economic assessment of three electricity-based reactor processes for production of liquid fuels and/or hydrocarbons from natural gas" by Technical Development Department of SNC Inc for CANMET, March 1985, DSS file 265Q.23440-3-9076.

Cooke, N.E., F.A.Asraf, H. Divanji, M. Konecny, P. Owerie, and T.Q. Quach, "Technical and economic assessment of produceing liquid fuels from natural gas via an electricity-based aceyelene process, Phase II" SNC Inc for CANMET, March 1986, DSS file 14SQ.23440-4-9146

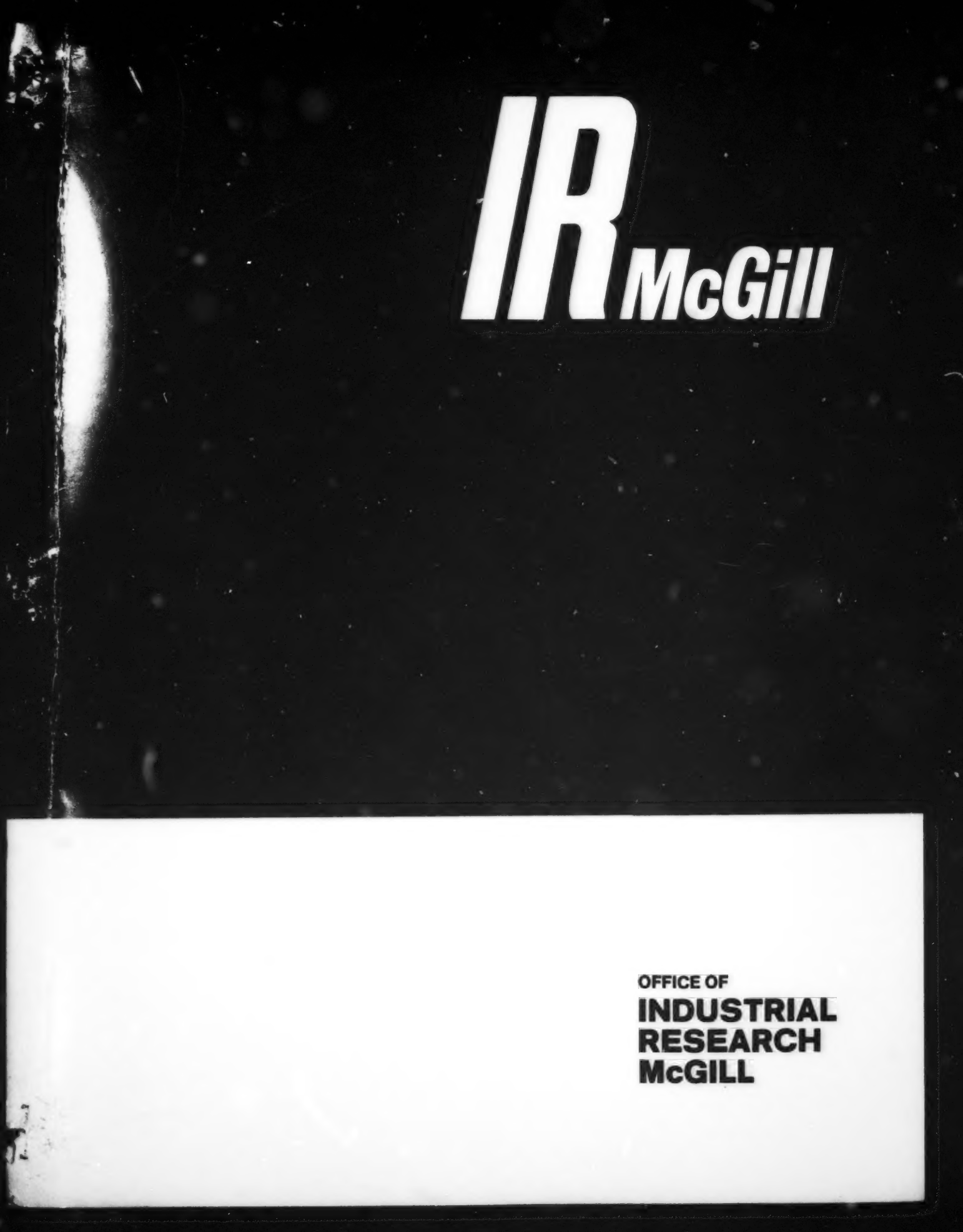
Table 1: Capital Cost Estimate for Plant to Treat 10 000 kg/h of CANMET residue in Hydrogen Plasma (based on SNC Phase II Report)

PROCESS AREA	Jan. 1986 $M Can.
acetylene production and product separation	24.26
total on site cost	24.26
steam generation	0.32
incineration (carbon black)	0.13
water treatment	0.08
electrical	12.25
steam cooling and process water	1.34
refrigeration	0.64
site preparation	1.60
sewer fire etc	0.34
air supply	0.12
product shipping	0.81
interconnecting pipe racks	0.50
sub total	18.14
direct capital cost	42.40
contingency	4.24
sub total	46.64
Indirect Capital Investment	
license and prepaid royalties	0.14
initial catalysts and chemicals	0.00
startup and other	1.40
working capital	1.40
land	0.09
Total capital investment	49.68

Table 2: Operating Maintenance and Production Costs as well as Product Cost for a plant treating 10 000 kg/h of CANMET Residue

Cost Item	Jan. 1986 $M Can.	%
electricity[1]	12.08	55.7
chemicals[2]	0.58	2.7
make-up water	0.03	0.1
royalties 10 years	0.49	2.3
labour, supervision, operating supplies	0.20	0.9
maintenance including labour	1.39	6.4
property taxes and insurance	0.70	3.2
overhead and administration	0.56	2.6
depreciation (straight line 20 years)	2.33	10.8
capital recovery (level over 20 years[3])	3.30	15.3
total production cost	21.67	100.0
Production cost of acetylene (assuming 77.75 kg/kg residue)	34.8 cents/kg	

1. Based on $.02/kWh and about 8.5 kWh/kg C_2H_2 formed
2. Primarily consumable scrubbing fluids
3. Uses assumptions of original SNC Phase I report



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FINAL REPORT

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TREATMENT OF CANMET COPROCESSING RESIDUES IN HYDROGEN AND STEAM PLASMAS

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TREATMENT OF CANMET COPROCESSING RESIDUES IN HYDROGEN AND STEAM PLASMAS

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INTRODUCTION

CANMET are developing a hybrid process for coal liquefaction and heavy oil hydrocracking which is known as "coprocessing". Finely ground coal particles are mixed with heavy oil and hydrogenated under high temperature and pressure. The resulting products are distilled to obtain distillates and residues. The distillates are further hydrotreated to meet various product specifications.

The disposal of residues from this process poses serious problems. Because these residues contain a high level of sulphur and ash, they have little commercial value and are considered to be toxic waste. Ash in the residue consists of relatively inert mineral matter and reactive metallic components that are added the feed as catalysts. If an inexpensive iron-based catalyst is used the disposal of the catalyst with the residue can be justified. However if a more active and more expensive catalyst is required, its disposal with the residue becomes economically unacceptable. The residues are solid at room temperature and only begin to flow at about 373 K. The entire residue stream could be burned in a power plant and the catalyst particles recovered in the fly ash, but the cost of building the power plant required may be prohibitive.

In this work, thermal plasma processes were to be assessed as a way of treating coprocessing residues. The objectives were to examine the feasibility of recovering the catalyst in a useful form while at the same time producing commercially attractive gases such as acetylene and heavier gases from the residues.

It had been demonstrated in a previous work (Kubanek et al 1986) that high conversions of heavy oil to acetylene and other gaseous products could be achieved in both hydrogen and steam plasmas. Even though that process was far from optimized, conversions to gas of up to 100% were achieved; with a hydrogen plasma, acetylene production was comparable to that achieved in the well-known Huels process. The ash from the completely reacted heavy oil was recovered primarily as a fine, dry, solid.

No work had previously been done with the specific residue form the CANMET process and the present project was undertaken to examine the both the gaseous product mix and the solid remains which would be retained following treatment in a hydrogen plasma. Because only small samples of residue were available from CANMET for testing a miniature reactor system was developed and used.

The results of the study, which were divided into work with both batch and continuous reactor systems, are described in this report. More details are provided in the M.Eng. theses of Bogdan Dlugogorski and Muftah El-Naas. The first thesis has already been submitted to CANMET as an interim progress report while the second, which deals with the continuous work will be submitted before the end of this year.

OBJECTIVES

The specific objective of the project were as follows:

PHASE 1 - to examine thermodynamics of the treatment of CANMET residue in hydrogen and steam plasmas and identify optimum reaction conditions.
- to design, build, and commission the induction plasma mini-reactor

PHASE 2 - to carry out batch reactions of CANMET residue in with hydrogen and/or steam containing plasmas to determine catalyst recovery, separation, and activity
- to carry out the continuous reaction of the residue in a multiparticle continuous system to determine product gas composition as function of operating parameters.

In the course of the project these objectives were modified slightly in agreement with Dr. M. Ikura of CANMET. Specifically, it was decided to base the continuous reaction study on a single stationary particle system in which the particle reacting surface was continuously renewed. In this way the reacting surface area could be better controlled and known. Catalyst activity was not examined because the process continues to use only the inexpensive iron-based catalyst. This need not be recycled.

THERMODYNAMIC ANALYSIS

Free energy minimization calculations were performed in which the CANMET residue organic component with a molar composition of $CH_{1.0601}N_{0.0135}S_{0.0172}O_{0.0412}$ and molecular weight of 14.46 g/mol was allowed to reach equilibrium at one atmosphere in various argon/hydrogen compositions and at different temperatures in the range 500 - 6000 K. The full details are given in Dlugogorski's M.Eng. Thesis. The analysis predicted that the major products would be methane and ethane at low temperatures and acetylene and C_2H (a radical which decomposes to acetylene) at medium temperatures (between 1200 and 4000 K). At higher temperatures, only gaseous carbon and monatomic hydrogen would be formed as the main products. These could condense as hydrogen and solid carbon.

A thermodynamic window existed between about 1000 and 4000 K in which conversion of carbon to acetylene and C_2H was of the order of 90% and was almost independent of the plasma gas composition. The oxygen in the residue was predicted to form primarily CO, while the sulphur would form H_2S. In the presence of steam plasma, the carbon would be recovered primarily in the form of carbon oxides which have little value. For this reason it was decided to work uniquely with argon or argon/hydrogen plasmas.

BATCH EXPERIMENTS

Apparatus

The plasma equipment consists of a high frequency power supply, control console for gases, an induction plasma torch, a single particle reactor system, a sampling train, and a suction probe (Figure 1). The induction power supply converts 3 phase, 60 Hz power into 4 MHz power which is delivered to the torch; it is rated at 30 kW. The flow of argon and hydrogen to the torch is measured and controlled by calibrated ± 2% rotameters.

A commercial plasma torch (TAFA Model 56) was used for the work. The plasma is generated within a water-cooled quartz tube surrounded by the 6 turn induction coil. The hot plasma exits the torch through a water-cooled copper nozzle. The plasma is swirl and wall stabilized. The plate power (power to the torch) is limited to between 4 and 14 kW; below this level the flame extinguishes and above it the quartz tube breaks. Between 4 and 7 kW, an inverted flame, characterized by a relatively cold central part and hot flame fringes is formed. This could be used because of excessive thermal gradients within the flame core.

Hydrogen could not be directly injected into the plasma torch because of the extremely high heat fluxes it causes to the quartz tube; these caused the tube to devitrify and crack in a few minutes. Hydrogen was thus injected through two diametrically opposed orifices in the torch exit nozzle. This had two undesirable effects: it cooled the tailflame and gave poor mixing if more than 35% hydrogen was injected. The concentrations used in the experiments were limited to 20% for which the deviation between the local and mean values in the tailflame were less than 5% of the measured value.

The water-cooled reactor was fabricated from a single piece of monel; it housed the crucible containing residue. Pyrometric and spectroscopic measurements were performed through a window in the upper section of the reaction chamber. The upper part of the reactor was 5.08 cm in inside diameter and 11.4 cm in length. The internal diameter could be decreased to 2.54 cm by adding a water cooled insert. The lower part of the reactor (2.54 cm in diameter and 5.08 cm in length) contained the reactor outlet (1.9 cm in diameter) and below that a cool stagnant region which accommodated the crucible prior to reaction. The molybdenum crucible (1.9 cm in length, 1.3 and 1.4 cm in inside and outside diameters) was mounted on a 0.32 cm alumina rod which moved vertically. The alumina rod was placed slightly off the reactor centre line to permit installation of the suction probe. The reactor was connected with flanges to the torch and to the heat exchanger.

Sampling Techniques

The gas samples were withdrawn from two locations: (1) from the exhaust gas stream leaving the reactor and (2) from the reactor chamber through the suction probe. The samples were taken at different positions but usually 5.5 cm below the top of the crucible. The gases were cooled either inside the probe or by passing through 12.2 m of stainless steel tubing (with diameter of 0.32 cm) submerged in an ice-water mixture, if samples were withdrawn at the reactor outlet. (In a number of runs made to test for the presence of light liquid hydrocarbons, the ice-water bath was changed for a dry ice acetone bath.) Then the gas was passed through a condenser and a filter to trap soot particles, and eventually sent through a rotameter to verify that the flow was constant. Subsequently the gas was either exhausted to the fume hood or collected in a plastic bag as an integral sample (Figure 2).

A water-cooled suction probe was designed to withdraw the hot gas from the reactor chamber and quench it at a rate of at least 0.4×10^6 K/s to reduce acetylene decomposition and at the same time to measure the gas inlet temperature using a W-5%Re/W-2%Re thermocouple.

Gas Analysis

Mixtures of permanent gases (H_2, CO_2, Ar/O_2, N_2, CO) and hydrocarbons (CH_4, C_2H, C_2H_4, C_2H_2) were separated isothermally using a two column system which consisted of a Porapak N (0.32 cm i.d. x 1.98 m) followed by a Molecular Sieve 5A column (0.32 cm i.d. x 2.74 m). The gas analysis was performed in the isothermal Fisher Gas Partitioner 1200 with the thermal conductivity detector and using 8.5% hydrogen in helium carrier gas.

Experimental Procedures

Before an experimental run, approximately 1.20 g of the residue was weighed into the crucible and melted to eliminate trapped air. The crucible was mounted on the alumina support rod and placed in the lower part of the reactor below the gas exit. The temperature in this part of the reactor reached about 480 K which was enough to melt the sample but too low to permit chemical reactions. The suction probe was positioned in the reactor and was not moved during the experiment. The reactor was attached to the torch, and the cooling water was allowed to flow. The reactor was purged with argon to remove any residual oxygen.

The plasma was initiated, and the argon flow and hydrogen flow rates and plasma power were adjusted. Extra argon was added through the reactor window shroud to prevent the deposition of soot. The alumina rod supporting the crucible was moved into the reaction zone and a stopwatch was started. Gas samples were taken in 1 cm^3 syringes with gas locks every 3 to 15 seconds. After 3 to 5 minutes the torch was turned off, the argon and hydrogen flows were stopped and the crucible was allowed to cool.

Immediately following an experimental run the composition of gas samples was determined on the gas chromatograph. The unreacted residue was removed from the reactor, separated into an upper and lower part, weighed, ground and prepared for further analysis. Soot samples were also taken.

Characterization of the CANMET residue

The analysis of the CANMET residue as well as the coal and vacuum bottoms used to feed the process are given in Table 1 below.

Table 1: Elemental Compositions of the CANMET Residue and the Feedstocks to the CANMET Process

Element	CANMET residue (%)	Forestburg Coal bottoms (%)	Cold Lake vacuum
Carbon	74.1[1]	64.04	83.4
Hydrogen	6.60[1]	3.87	9.69
Sulphur	3.43[1]	0.53	5.84
Nitrogen	1.81[1]	1.65	0.45
Oxygen	4.10[1]	20.41[4]	0.68[4]
Ash	9.68[2]	9.5	-

1 elemental analyzer
2 ashed at 1050 K to constant mass
3 From Rahimi et al. (1989)
4 By difference

The residue starts to flow at 430 K and it may be pumped at 500 K. At this temperature its viscosity is estimated to be 1200 mPa s. The residue was analyzed on an elemental analyzer for carbon, hydrogen, nitrogen and sulphur; the sulphur analysis includes both organic and inorganic sulphur. With exception of oxygen, the errors are less than 0.03%.

The elemental abundances in the CANMET residue result from by the elemental composition of the Forestburg Coal and the Cold Lake vacuum bottoms. Sulphur, nitrogen and oxygen are preferentially retained in higher boiling fractions from the CANMET process and in the remaining residue (Rahimi et al., 1989). The C/H ratio of the residue (0.94) is between those of Forestburg coal (1.37) and the Cold Lake vacuum bottoms (0.72). It corresponds to the C/H ratio of hydrocarbons that distil between 478 and 798 K,

are soluble in methyl-tert-butyl ether and are characterized by high aromaticity and high nitrogen content (Rahimi et al., 1989). Thus it appears that the organic part of the CANMET residue contains a highly condensed aromatic structure. This was further corroborated by investigating the solubility of the residue in different solvents.

The solubilities of the residue in tetrahydrofuran (THF), toluene and pentane were found to be 72.1, 63.3 and 46.3%. THF is a powerful solvent for a wide spectrum of synthetic and natural materials (Mellan 1977). It dissolves not only aliphatic, alicyclic and aromatic hydrocarbons (as does pentane) but also dissolves heterocyclic aromatic compounds more efficiently than does toluene. Moreover the aromaticity of toluene solubles is higher than pentane solubles and smaller than THF solubles. According Rahimi et al (1989), the solubility of the Cold Lake vacuum bottoms in pentane was 76.2%. Therefore the structure of the CANMET vacuum residue is more aromatic than the structure of the Cold Lake vacuum bottoms, especially since there is a substantial difference in the solubility of the residue in pentane and in toluene. In fact the CANMET residue can even be more aromatic than the original coal since simple aliphatic and alicyclic hydrocarbons elute first during the distillation. Moreover 8.8% of the residue is soluble in THF but not in toluene and about 15% of the organic part of the residue is not THF soluble at all. Again this indicates that the residue contains high proportion of condensed and complex aromatic hydrocarbons which incorporate nitrogen, sulphur and oxygen in their structure.

To determine the amount of ash in the residue, a 2 g sample was placed in a crucible and ashed in a furnace at 1048 K to constant mass. The ashing of THF insolubles yielded 34.57% ash, i.e. 9.65% on the basis of the original residue. This may be compared with 9.68% from Table 1 to show small error in those results.

If the residue is ashed at 1273 K for a few hours to a constant mass all metal oxides are transformed to their highest and known levels of oxidation. Table 2 shows the analysis of the ashed CANMET residue performed by the X-ray fluorescence (XRF). It was reported that the Cold Lake vacuum bottoms contain V (235 ppm), Ni (93 ppm) and Fe (18 ppm) (Rahimi et al., 1989). Although the presence of some metals is beneficial in the coprocessing of coal and vacuum bottoms since they act as catalysts (e.g. nickel, vanadium, iron sulphate and chromium oxide) the assembly of the inorganic compounds in the residue has an overall negative effect on the conversion of the residue to acetylene in the plasma. In addition, the amount of the high temperature ash is less than the amount of the inorganic part in the residue. Thus the amount of hydrocarbons in the residue that could be produced by reaction in the plasma is less than derived from the carbon and hydrogen content in Table 1. Moreover, the mineralogy of the original coal and the residue is very different from the mineralogy of the ash.

An X-ray diffraction study was performed to gain further insight into the mineralogical content of the residue. The mineral content of the residue was concentrated by dissolving a significant percentage of the organic part of the residue in THF and then carrying out a low temperature plasma ashing to preserve the oxidation state of the sample minerals. Some amorphous carbonaceous material was not removed. Among the minerals present trigonal

quartz was the easiest to identify and gypsum, anhydrite, hemihydrate (bassanite) and hematite were also seen. It is possible that hematite, anhydrite and to a certain extent bassanite are artifacts from the plasma ashing in LTA. In general, carbonates (dolomite, calcite, ankerite), feldspar (orthoclase, albite), clay (kaolinite, illite), siderite, pyrite and iron sulphate are probably present but they could not be definitely identified.

Table 2: Results from the XRF Analysis of the Ashed CANMET residue

Compound	Content
SiO_2	36.99%
Fe_2O_3	22.57%
Al_2O_3	18.42%
CaO	15.57%
MgO	3.52%
Na_2O	0.68%
TiO_2	0.47%
K_2O	0.29%
MnO	0.17%
V	5302 ppm
Ni	3852 ppm
BaO	3512 ppm
P_2O_5	960 ppm
Cr_2O_3	622 ppm

Gas Composition and Conversion to Gaseous Products

A total of 26 different experimental conditions of plasma gas temperature (2100 - 4450 K) and hydrogen concentration (0 - 20%) were used with at least one replicate at each hydrogen concentration and five replicates at 3390 K and 10% H_2.

Acetylene, ethylene, methane, carbon monoxide and hydrogen were produced in greatest quantity. Trace amounts of ethylene were detected in only a few experiments but this gas was never observed in the integral samples. The concentration of hydrogen sulphide was always below 10 ppm.

The mean plasma gas temperature in the tailflame was measured by calorimetry and emission spectroscopy on the rotational band of C_2 at 516.5 nm. The latter measurements confirmed the results of the calorimetric experiments and showed that there was essentially no thermal gradient in the core of the jet in which the crucible was located.

Two-wave length pyrometric measurement of the crucible in the absence of reaction

showed that the crucible reached only about 50% of the plasma gas temperature. During reaction, when the crucible surface was contaminated with soot, its temperature would be even less.

The time required for reaction, as determined by the evolution of gaseous products, depended somewhat on the plasma gas temperature but was less than 110 s for experiments with pure argon plasma and 85 s for runs with 20 % hydrogen/argon plasma. Conversion of the residue was not complete at the end of this time but the rate of reaction was so slow that reaction rates could no longer be measured. This was because the most volatile components had been removed. Radiant heat losses from the crucible kept its temperature well below the plasma temperature and thus prevented complete reaction.

The conversion of carbon in the residue to acetylene (Figure 3) was about twice as high in 10 and 20 % hydrogen plasmas (23 %) as in pure argon plasma (14 %). There was no increase in the acetylene production once the hydrogen content in the plasma gas reached 10 %. Thus similar results would be expected in pure hydrogen plasmas. Moreover, the conversion to acetylene in argon/hydrogen plasmas as a function of temperature exhibited a broad maximum at around 3200 K. This trend agrees with the results of the thermodynamic calculations; however the maximum conversion is lower than predicted.

The conversion of carbon to ethylene (Figure 4) and methane (Figure 5) was higher in 20 % than in 10 % hydrogen plasmas but much smaller than the conversion to acetylene in all cases. The treatment in pure argon plasma produced ethylene and methane only below 3000 K. These results are in agreement with the thermodynamic predictions.

The production of carbon monoxide (Figure 6) depends only on the plasma gas temperature and increases with temperature. The emission of CO may be divided into two stages. Below 2800 K organic oxygen is removed by cracking and the conversion of oxygen to CO is approximately constant. Above 2800 K, inorganic oxygen leaves the residue because of mineralogical transformations especially the removal of oxygen from calcium sulphate. It is interesting to note that the conversion of oxygen in the residue to gaseous form is higher than the conversion of carbon to gaseous products such as acetylene, ethylene and methane (Figure 7) even at low temperatures. This must be due to the reduction of metal oxides by carbon to form carbon monoxide and the relative involatility of the carbon in the residue.

Effect of the Gas Residence Time

The residence time of the gas was calculated on the basis of the average flame temperature at the torch exit and the reactor volume below the top of the crucible. In some experiments, a water-cooled insert with an inside diameter of 2.54 cm was placed in the reactor to reduce the reactor volume. The gas samples were withdrawn either from the exhaust gases at the reactor outlet or through the suction probe 5.5 cm below the top of the crucible. These combinations of reactor volume and sampling techniques allowed the gas residence

time to be varied between 0.36 and 52 ms.

No measurable difference was detected in the conversion of carbon to acetylene suggesting that either the decomposition of acetylene occurs within the crucible or that the degradation of acetylene to soot may be slower than previously reported in the literature (Melamed et al. 1965). The quench rate in the water-cooled probe was determined experimentally to be to be greater than 0.4×10^6 K/s which should have been more than enough to preserve any acetylene formed as computed by Sundstrom and DeMichiell (1971); they required 0.13×10^6 K/s between 1500 and 600 K and a point quench rate of 0.31×10^6 K/s at 1150 K.

Isolation of Liquid Hydrocarbons

Even when cooling the reactor exhaust gases with a dry ice-acetone mixture at 216 K, no liquid hydrocarbons were isolated. It is known that during decomposition of long chain paraffins and high molecular weight cycloalkanes and aromatics to light unsaturated hydrocarbons in the plasma the conversion to liquid hydrocarbons is around 2.0% and 12.0% respectively (Baronnet et al. 1987). The CANMET residue contains heterocyclic complex aromatic hydrocarbons rather than aliphatics and cycloalkanes. However, as determined by (Baumann et al. 1988) the latter group of compounds decompose in plasma to form condensable compounds called tars or primary volatiles. In the plasma gas these primary volatiles undergo further cracking resulting in the production of acetylene. Thus, the hydrocarbon composition of the CANMET residue appears to be the reason for the absence of of liquid hydrocarbons in the product.

Behaviour of the Unreacted Residue

The residue left in the crucible after reaction accounted for between 40 and 50 % of the initial mass and this decreased as the plasma gas temperature increased. The effect of plasma gas composition gave no definite trends. The unconverted residue contained practically no hydrocarbons which were soluble in tetrahydrofuran. This implies that the aliphatic, alicyclic and part of aromatic hydrocarbons were cracked and the organic part of the residue contained only condensed aromatic structure with heteroatoms which are not soluble in THF.

The amount of ash left in THF insolubles increased slightly with increasing temperature reaching 25 % at above 4200 K. This indicates that at higher gas temperatures inorganic elements become more concentrated in the crucible whereas carbon is preferentially removed into the gas phase. This is expected since increasing gas and crucible temperatures give faster and more complete pyrolysis.

After ashing, the unconverted residue, was analyzed for iron, aluminum, vanadium and nickel by atomic absorption. Vanadium, iron and nickel were selected for analysis for their

potential to be used as catalysts in the CANMET process. However, no significant variations in the contents of Fe, Al, V and Ni were observed either with temperature or composition of the plasma gas. It is concluded that further separation is required to recover the catalyst from the unreacted residue.

The hydrogen content of the unreacted residue varied greatly depending on the position of the unreacted residue in the crucible as can be seen in Figure 8. For the carbon and hydrogen analyses the unconverted residue was divided into two samples: one representing the top portion of the unreacted material (which was directly exposed to the plasma flame) and the bottom part (which remained at approximately crucible temperature). The results showed that the top part of the unreacted material contains less hydrogen, often by a factor of up to three. There appeared to be a decrease in residue hydrogen content as the plasma gas temperature increased and more hydrogen was removed in hydrogen containing plasmas than pure argon plasmas at the same temperature.

The nitrogen and the sulphur content of the unconverted residue varied little with position in the crucible. Both nitrogen and sulphur become more concentrated in the unreacted residue; the original nitrogen and the sulphur contents were 1.18 and 3.43 % respectively while final values averaged 1.37 and 4.28 respectively. This again indicates that the aliphatic, alicyclic and aromatic hydrocarbons are pyrolysed first and those which contain heteroatoms, such as N and S, decompose during the later stages of pyrolysis; their decomposition may not be complete. In addition, the organic and inorganic sulphur is retained in CaS.

The distribution of oxygen in the crucible was similar to that of hydrogen. Inorganic oxygen was released from the calcium and magnesium salts by the thermal decomposition or during the fixation of sulphur and from kaolinite by dehydration. The presence of the organic oxygen may actually enhance the initial cracking since the oxygen would be preferentially removed from the hydrocarbon structure.

Finally, X-ray diffraction analyses were performed for selected samples. Gypsum ($CaSO_4 \cdot 2H_2O$) and bassanite ($CaSO_4 \cdot 1.5H_2O$), which were the easiest to observe, converted initially to anhydrite and then to $CaSO_3$ and eventually to calcium sulphide (CaS). Thus the following mechanism is suggested for the fixation of sulphur during the plasma treatment;

$$CaSO_4 \cdot 2H_20 \rightarrow CaSO_4 \cdot 1.5H_20 \rightarrow CaSO_4 \rightarrow CaSO_3 \rightarrow CaS$$

The fixation of sulphur in the residue was already hinted by the lack of H_2S in the outlet gases. Scanning electron microscopy showed that after reaction, the sulphur was evenly distributed in the sample and not associated with single crystals as before reaction. It seems that the inorganic minerals were initially melted (or partially melted) during the reaction and they did not appreciably recrystallize due to the rapid cooling of the crucible after the experiment was stopped. In addition the carbonates (dolomite, calcite) which easily decompose to calcium and magnesium oxides during the plasma treatment might have also

participated in fixing the sulphur, as follows (Ibarra et al., 1989);

$$CaO + H2S \rightarrow CaS + H_2O$$

The transformations of the iron bearing compounds could not be resolved by X-ray powder diffraction. For example, it appears that iron sulphate decomposes only at higher temperatures. Although the production of iron would be expected it could not be confirmed due to the low resolution of the unashed XRD traces and the oxidizing character of the low temperature asher (the unconverted residue was not ashed to avoid any chemical changes; the plasmas used were inert or reducing while LTA is strongly oxidizing).

CONTINUOUS FEEDING EXPERIMENTS

Experimental Apparatus

All parts of the equipment except the reactor, residue feeding system were essentially the same as those used for the batch experiments.

The reactor was designed to meet the following criteria: (1) very low gas residence time to avoid decomposition of gaseous products such as acetylene; (2) low Reynolds number flow over the reacting residue surface to simulate the reaction of a micro droplet falling in a plasma flame; and (3) continuous feeding of the hot residue to present a known surface area.

The reactor is shown in Figure 9. It was water-cooled with an inside diameter of 2.54 cm and a length of 10 cm. It had two diametrically opposed gas outlets (1.27 cm in diameter) and a viewing port (1.91 cm in diameter) located 2 cm below the entrance of the reactor. The gas exhausts were located in the top part of the reactor to shorten gas residence time and to avoid heating the overflow of residue. The viewing port was kept clear by a shroud of argon. The reactor joined to the plasma torch with an O-ring seal tightened by six bolts.

The residue was fed to the reactor by a syringe pump consisting of a steam-jacketed stainless steel syringe, a variable speed d.c. motor and a gear box. The syringe volume was 100 cm^3, and the pump could deliver flow rates ranging from 2 to 10 g/min. Steam at 860 kPa was used to heat the syringe and keep the residue in liquid form at about 450 K. The residue was introduced into the reactor through an inconel tube 6.35 mm in diameter and 12 cm in length. The tube was made with a molybdenum tip (1.27 cm in diameter) to provide a large and well-defined contact area between the plasma flame and the residue; this also prevented the flame from extending further down to the unreacted residue. The fed residue flowed into the reactor in a fountain-like form creating a continuously renewed surface that was in complete contact with the plasma flame. The lower part of the reactor (below the residue feed) provided a low temperature zone for accumulation of the unreacted residue in a stainless steel collection cup.

The bottom of the reactor also contained a support system for the feeding tube. The system was designed to allow the tube to move vertically for positioning. It was steam heated to avoid solidification of the residue. The feeding tube was connected to the syringe pump through a short piece of teflon tubing 0.794 mm inside diameter. The teflon tube was necessary to electrically isolate the reactor from the feeding system which was grounded. The teflon tube was heated during experiments using an air heating gun.

Experimental Procedures

The reactor and feeding probe were attached to the plasma torch. A sample of the CANMET residue (about 120 g) was liquified by heating it in a 250 ml pyrex glass beaker in a microwave for about 15 minutes. The sample was then poured into the syringe which was connected to steam lines to keep the residue at a constant temperature. The syringe was connected to the feeding tube by the teflon tubing, and argon gas flow was started to purge the system for about 1 minute. The plasma was initiated and adjusted to the desired plate power. Hydrogen was then injected into the plasma tailflame at the desired flow rate and the residue flow to the reactor was started.

Once the residue was visible through the viewing window, a stop watch was started, and gas samples were taken every 30 seconds for about 3 minutes. The plasma torch, the residue flow and the stop watch were stopped at the same time. The power supply and the cooling water flow were turned off, and the gas samples were taken for analysis. The unreacted portion of the residue was weighed and collected in sampling vials for later analysis. Argon was the principal plasma gas used in all experiments, and its flow rate was fixed at 32.5 litres/min measured at 283 K and one 101 kPa. The argon was injected 64% axially and the remainder axially into the plasma torch. As with the batch experiments described previously, hydrogen was injected into the tailflame at concentrations between 0 and 23 mole per cent.

Gas samples were withdrawn using a water cooled suction probe and analyzed using the same gas chromatographic technique described for the batch experiments.

Experimental Results: Introduction

The objectives of the continuous study were firstly, to design and build a laboratory-scale plasma reactor with a continuous residue feeding system and secondly, to use it to study the continuous pyrolysis of CANMET coprocessing residue in argon and argon/hydrogen plasmas. The effect of plasma gas composition, temperature and residue flow rate on the composition of gaseous pyrolysis products and the unreacted residue after treatment were to be examined. Because of the operating limitations of the system, the conversion of the residue was low and so it was essentially unchanged in the continuous reactions. The work thus concentrated on the behaviour of the gaseous pyrolysis products. A few batch runs

were carried out in which a more complete reaction of the residue was attempted. These will be described later.

All experimental results presented here are based on steady state conditions i.e. when the concentrations of product gas was not a function of operating time.

Effect of Sampling Location on Product Composition

The only gaseous hydrocarbons detected were acetylene, methane and ethylene; as in the batch experiments, acetylene was the major product. The concentration of these products in the exhaust stream was found to vary with sampling position as shown in Figure 10. The first sampling point was located inside the reactor (just before the gas exits the reactor), while the second was located near the inlet of a 1.27 cm diameter exhaust tube where the gas flow was turbulent (Re >2600). Subsequent points were further along this tube.

The variations in product composition due to sampling location were attributed to two factors: residence time and mixing. The low concentrations of hydrocarbons measured at the first sampling point were due to incomplete mixing of the plasma gas and the pyrolysis products formed, because of the flow pattern of the plasma gas over the reacting residue. Another possible reason might have been insufficient reactant residence time to form the acetylene and ethylene, (Gehrmann et al, 1977), although this was probably a minor effect. The decline in concentration beyond the second sampling point was attributed to decomposition to carbon black. Hydrocarbons decompose if the reaction is not quenched, and this is more obvious with acetylene, since it is less stable at low temperature than the other two gases. The sampling positions shown in Figure 10 will be referred to throughout this section as sampling points 1, 2, 3 and 4. The quench rates were of the order of 10^6 K/s.

Importance of Heat Transfer to Residue

Before discussing the experimental results of varying the plasma gas composition, it is important to look at heat transfer from the plasma tailflame to the residue. Because the hydrogen was added to the plasma tailflame, it lowered the plasma temperature at a constant torch power (see Figure 11). At the same time, the thermal conductivity of the plasma increased, because hydrogen has a much higher thermal conductivity than argon. It was the interaction of these two opposing effects which determined the rate of heat transfer to the reacting residue. A simple analysis was carried out to predict the variation of convective heat transfer to the liquid residue as the hydrogen composition was changed at constant plasma power.

Radiative heat transfer was assumed to be constant since the greatest part of the radiant flux comes from the plasma fireball which contains only argon at constant temperature. Moreover, the radiant flux is much smaller than the convective heat transfer in the present situation.

The Nusselt number for the residue was estimated using the Whitaker equation for heat transfer to a sphere i.e.

$$Nu = 2 + (0.4\,Re^{0.5} + 0.06\,Re^{0.67})Pr^{0.4}\,(\mu/\mu_s)^{0.25}$$

The residue on the tip of the feeding tube was assumed to be a hemisphere with a diameter equal to the tip diameter. Since the residue surface was continuously renewed, its temperature was considered to be fixed at about 200 C. All fluid properties except the gas surface viscosity were estimated at the plasma temperature. A plot of the calculated heat transfer versus plasma gas composition is shown in Figure 12. The profile shows a maximum between 10 and 15% hydrogen. Lower rates of heat transfer are predicted at low hydrogen concentrations (because of lower thermal conductivities) and at high hydrogen concentrations (because of the lower plasma temperatures).

The effect of Plasma Gas Composition and Temperature on Residue Conversion and Product Composition

Plots of residue conversion (Figure 13) and acetylene concentration (Figure 14)versus hydrogen concentration at constant residue flowrate and plasma power have the same general shape as Figure 12. This suggests that both the rate of residue pyrolysis and the rate of acetylene formation are strongly linked to heat transfer.

The formation of gaseous products may proceed by three mechanisms; direct pyrolysis on the residue surface, evaporation followed by gas phase pyrolysis and finally the ejection of fine droplets of residue (by surface boiling) followed by heterogeneous reaction of these droplets in the gas phase. Although the surface area of the droplets is very large, the degree of reaction is limited by the very short gas residence times in the reactor system at low Reynolds numbers (leading to poor heat and mass transfer rates). Their contribution to the gaseous products reaction is thus expected to be less than that of the other two mechanisms. They would be redeposited as unreacted soot.

The behaviour of the carbon which left the residue surface was examined by plotting the ratios of carbon converted to acetylene, methane and ethylene to the amount of carbon removed from the residue versus plasma gas composition in Figure 15. The numerators of these ratios were obtained by measuring gas compositions and flow rates during experiments. The denominators were determined knowing the residue feed rate, carbon composition and reaction time as well as the mass of unreacted residue collected in the cold section of the reactor after the experiment and its carbon concentration. The carbon which does not appear in the gaseous products must appear as soot. This soot may have come from either unreacted droplets as described above or carbon black from the decomposition of gaseous products.

The shape of the curve of Figure 15 shows that at low and high hydrogen concentrations, the conversion of carbon to gaseous products is high, whereas at the intermediate hydrogen concentrations, where heat transfer is highest, the conversion to gaseous products is less. This is exactly what would be expected because the droplets (which contribute little to the gaseous products) would be formed most readily when boiling of the residue is most vigorous.

The above argument was corroborated by the analysis of the soot collected from the reactor exhaust walls. Table 3 compares the composition of the soot with that of CANMET residue. A comparison shows that the carbon content of the soot is higher while the hydrogen content is lower than that of the residue. This suggests that at least part of the particulates formed resulted from the decomposition of gaseous products. The carryover of nitrogen and sulphur is clearly due to the presence of ejected droplets.

Table 3 : Elemental Analysis of Soot and CANMET Residue

Element	Soot	CANMET Residue
carbon	92.8	79.3
hydrogen	1.63	6.33
nitrogen	0.67	1.24
sulphur	1.99	2.05

Concentrations in weight per cent

Effect of Plasma Temperature

The effect of plasma temperature was investigated by varying the input power to the plasma torch while keeping plasma gas flow rate and composition (20% H_2) constant. Gas samples were withdrawn at sampling point 2 (3 cm from center of reactor). At this sampling position the gas temperature is lower than the initial plasma temperature. Usable plasma powers were limited to between 9 and 14 kW. The conversion of residue increased with increasing plasma temperature, as is shown in Figure 16, but the fraction of carbon converted to hydrocarbon gases decreased beyond 3000 K as shown in Figure 17. This is due to two effects. The thermodynamic analysis shows that hydrocarbon gases, especially acetylene, become increasingly unstable above 3000 K and this was also observed experimentally (see Figure 18). This would cause most of the gaseous carbon to precipitate as carbon black if the quench were sufficiently rapid. In addition, the amount of carbon ejected as droplets would be expected to increase with increasing heat transfer rates due in this case to the increase in temperature driving force. The temperatures below 2700 K where conversions to acetylene are expected to decrease for thermodynamic reasons could not be tested due to torch limitations.

Effect of Residue Flow Rate

The syringe pump used for feeding the residue had a flow rate range of 2 to 10 g/min. Only a fraction of this range could be used in pyrolysis experiments. At low flow rates (or moderate flow rates with high power plasmas), the residue pyrolysed rapidly creating a crust of solids on top of the feeding tube. This crust prevented efficient contact between the plasma gas and the residue resulting in little further reaction. Operation at high flow rates was limited by the size of the reactor; the unreacted residue collection cup in the lower part of the reactor filled before the system could reach steady state.

Experiments were conducted at flow rate between from 6 and 9 g/min. A hydrogen concentration of 8% and a plasma gas temperature of 3250 K were used. Both the conversion of residue and the concentration of acetylene decreased as the residue flow rate increased as is shown in Figures 19 and 20.

Batch Experiments for Complete Pyrolysis

The continuous pyrolysis experiments were intended to look at rate limiting steps and product mix and thus were not designed to achieve high conversions. A few batch experiments were carried out to investigate the feasibility of completely reacting the organic part of the residue. A small molybdenum crucible (0.635 cm in diameter and 1 cm in depth) was used; the crucible was connected to a ceramic support by a thin stem to minimize heat loss. Small samples of residue were treated at different plasma temperatures and plasma gas compositions for about 15 minutes. The amount of residue reacted depended on the operating conditions and the original size of the sample. The highest conversion was achieved for very small samples at high plasma temperatures. As in the case of the batch experiments which used larger crucibles, part of the unreacted solids created a hollow dome on top of the crucible while the remainder stuck to the bottom and walls of the crucible. The hollow dome was black and contained much carbon. The part within the crucible appeared shiny and metallic when removed from the crucible. Analysis by X-ray diffraction of samples of this solid showed that it had little carbon, and the only recognizable compound it contained was iron sulphide (FeS).

Even the miniature crucible used here suffered massive cooling by radiation and as a result reached temperatures of no more that 2030 K. At this temperature, about 77% of the carbon contained in the residue sample was gasified. The material in the bottom of the crucible was essentially carbon free so that the carbon which remained may have been due to redeposition of carbon from gaseous products.

CONCLUSIONS

1. A thermodynamic analysis of the treatment of CANMET residue in hydrogen plasmas suggested the major reaction products would be acetylene and C_2H radical in the temperature range 1000 - 4000 K. Carbon conversions to these products of the order of 90% were predicted.

2. Batch tests demonstrated the production of acetylene, ethylene, and methane but at lower conversions (40 - 50%). This was because the crucibles holding the crucible in the plasma flame were cooled by radiation and thus the very high temperatures used in the simulations could not be reached. Reducing the crucible size in a second series of experiment improved conversions. Maximum conversions to acetylene and ethylene occurred between 2500 and 3000 K in good agreement with thermodynamic predictions.

3. Because of the low residue temperature, carbon in the unconverted residue reacted little or not at all with hydrogen from the plasma gas. It may be concluded that the treatment of the CANMET residue consists of two stages: (1) heterogeneous reactions inside the crucible which include the pyrolysis of the hydrocarbons and the transformation of the mineral content of the residue and (2) homogeneous reactions between the gas products from the pyrolysis and the plasma gas.

4. Hydrogen in the plasma gas improves heat transfer rates (because of its high thermal conductivity) and in addition it takes part in gas phase reactions improving the acetylene yield.

5. The oxygen originally in the residue was removed as carbon monoxide. The removal of sulphur as hydrogen sulphide was very low since the sulphur became fixed in the ash as CaS. Nitrogen became more concentrated in the unconverted residue ash.

6. The continuous stationary particle experiments demonstrated that the reaction is heat transfer controlled at least until all volatiles have been removed. The product mix was similar to that obtained in batch experiments and predicted by thermodynamics.

7. At high heat transfer rates, very small droplets were ejected from the liquid residue surface by surface boiling. These reacted to only a small extent because of the short gas residence times used in the work.

8. Considerable quantities of soot were formed in both the batch and continuous experiments. These were a mix of partially reacted ejected droplets and carbon black formed by the decomposition of gaseous products.

9. No light liquid hydrocarbons were isolated despite cooling the product gases to 216 K in a dry ice - acetone bath. This was attributed to the hetercyclic complex aromatic hydrocarbon content of the residue.

IMPLICATIONS FOR A PLASMA RESIDUE TREATMENT PROCESS

In an industrial process the residue would be atomized to small droplets (30 - 100 microns) and contacted with a pure hydrogen plasma. The normal contacting scheme is cocurrent flow. The droplets would remain at their boiling points as the volatile components of the residue are removed. The volatiles would pyrolyse and react in the gas phase to produce acetylene and other gaseous hydrocarbons. Once the volatiles are removed, further carbon removal would be possible only through evaporation of the carbon, gasification by the oxygen contained in the mineral components of the residue, or surface reaction with hydrogen.

Although the rates of reaction which would be expected in this initial phase could be predicted with reasonable confidence from the results presented in this report, we presently can make no predictions on the reaction rate of carbon in the ash with hydrogen.

Two types of separation would have to be carried out in the process. Firstly, the gaseous products must be separated from the solids, and secondly, the ash or mineral content must be separated from the carbon black formed from hydrocarbon decomposition. The first separation is easily accomplished by standard technology. The second separation is expected to be far more difficult. Because of the large size distributions normally associated with atomization, some gaseous product decomposition may already have started while residue reaction is still not complete. This suggests that some deposition of carbon black on ash particles is to be expected.

The cost of the plasma part of the process can be fairly easily established from preliminary heat and mass balances. However, the cost and indeed the feasibility of the ash-carbon black separation process cannot be evaluated with any certainty without further experimental work. This work would have to establish the degree of conversion and form of solid products which could be obtained in a pilot scale atomized reactor system working with a pure hydrogen plasma. This type of study was not feasible in the present work because of the high cost and very limited availability of residue for tests.

We will provide a preliminary cost estimate of the plasma cost of the proposed process in an addendum to this report. If this part of the cost of treating the residue appears viable, a more complete technoeconomic assessment supported by further experimental work will be proposed. That assessment is however outside the scope of the present project.

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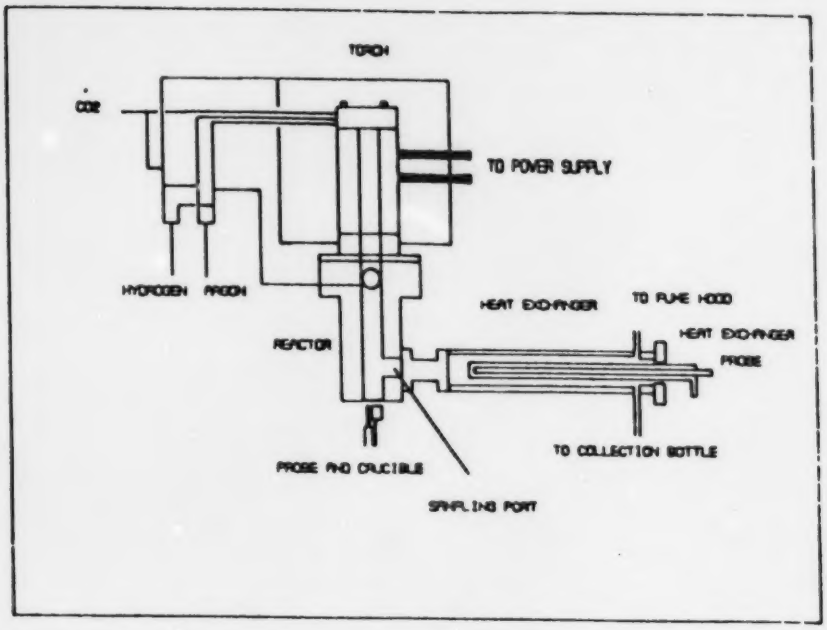

Figure 1: Experimental Apparatus for Batch Experiments

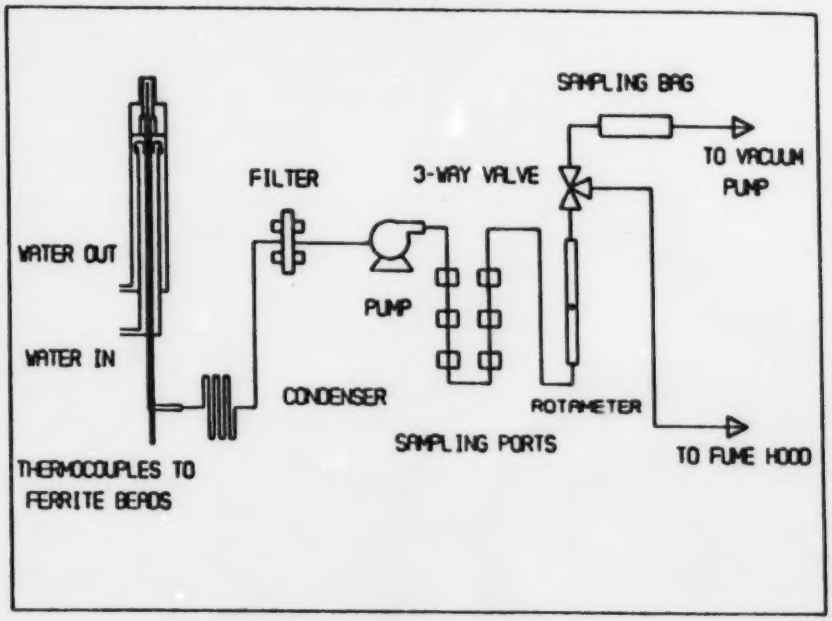

Figure 2: Probe and Sampling Train

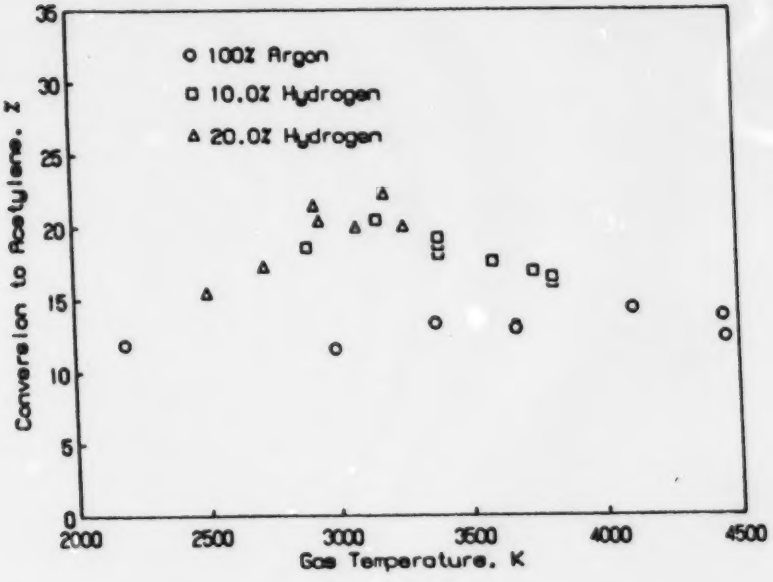

Figure 3: Conversion of Carbon in the CANMET Residue to Acetylene (Argon Flow = 20.81 g/min Radial and 37.22 g/min Swirl, Hydrogen Flow = 0.32 or 0.73 g/min to the Tailflame)

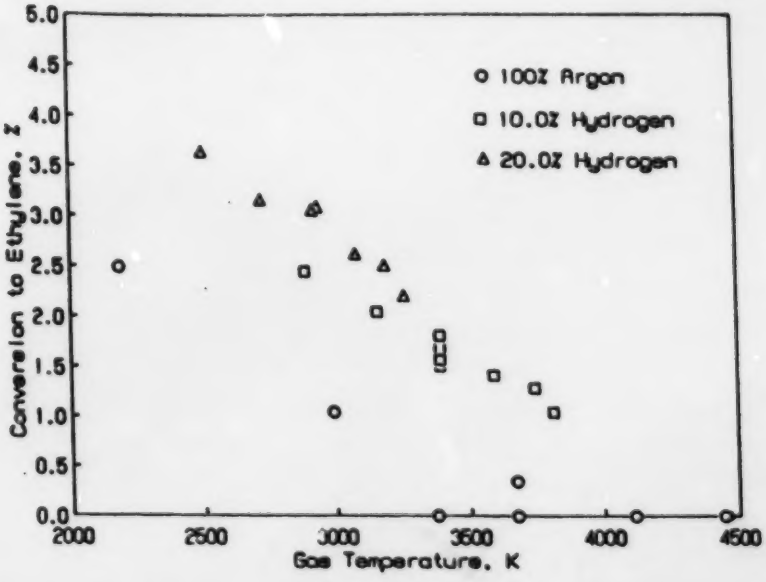

Figure 4: Conversion of Carbon in the CANMET Residue to Ethylene (Argon Flow = 20.81 g/min Radial and 37.22 g/min Swirl, Hydrogen Flow = 0.32 or 0.73 g/min to the Tailflame)

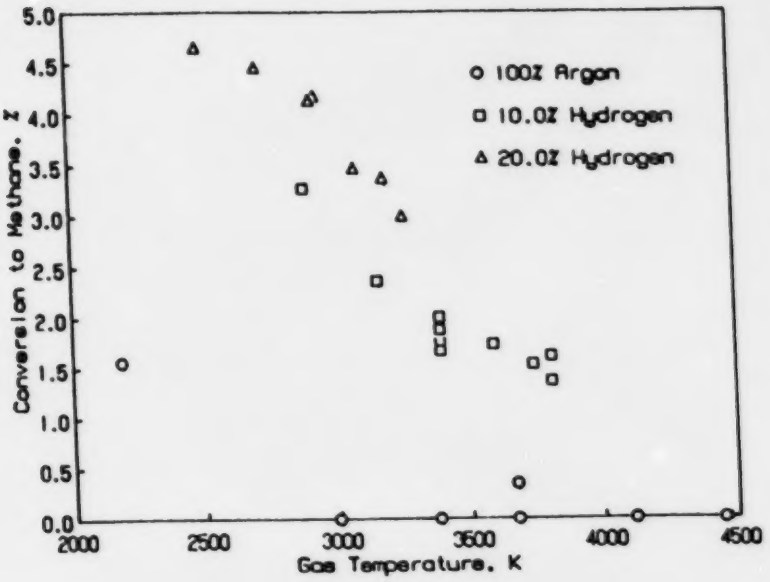

Figure 5: Conversion of Carbon in the CANMET Residue to Methane (Argon Flow = 20.81 g/min Radial and 37.22 g/min Swirl, Hydrogen Flow = 0.32 or 0.73 g/min to the Tailflame)

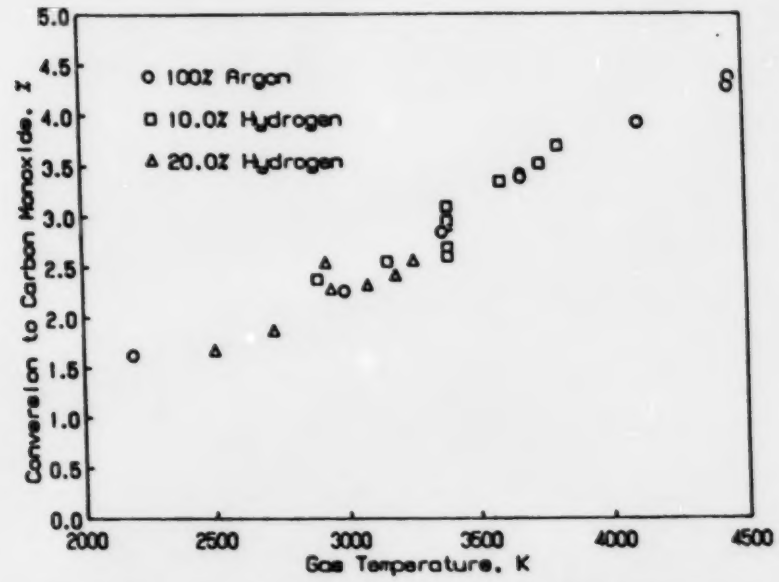

Figure 6: Conversion of Carbon in the CANMET Residue to Carbon Monoxide (Argon Flow = 20.81 g/min Radial and 37.22 g/min Swirl, Hydrogen Flow = 0.32 or 0.73 g/min to the Tailflame)

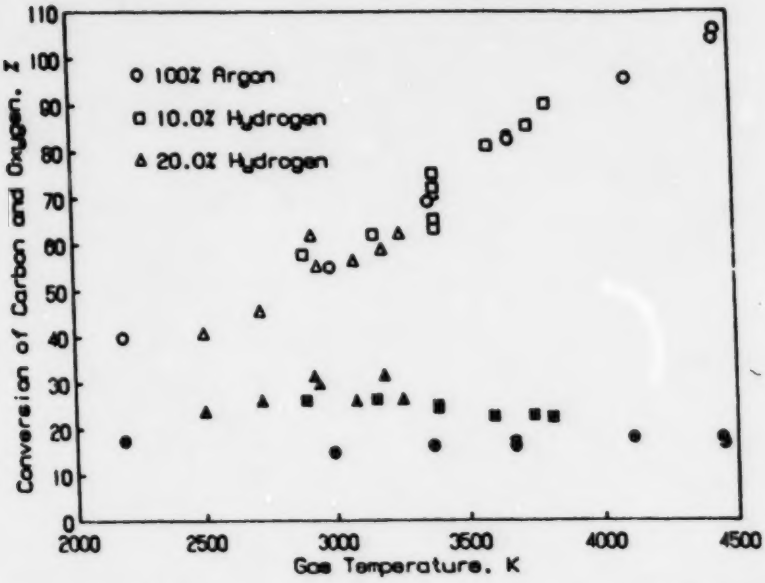

Figure 7: Conversion of Carbon and Oxygen in the CANMET Residue to Gaseous Products (Argon Flow = 20.81 g/min Radial and 37.22 g/min Swirl, Hydrogen Flow = 0.32 or 0.73 g/min to the Tailflame)

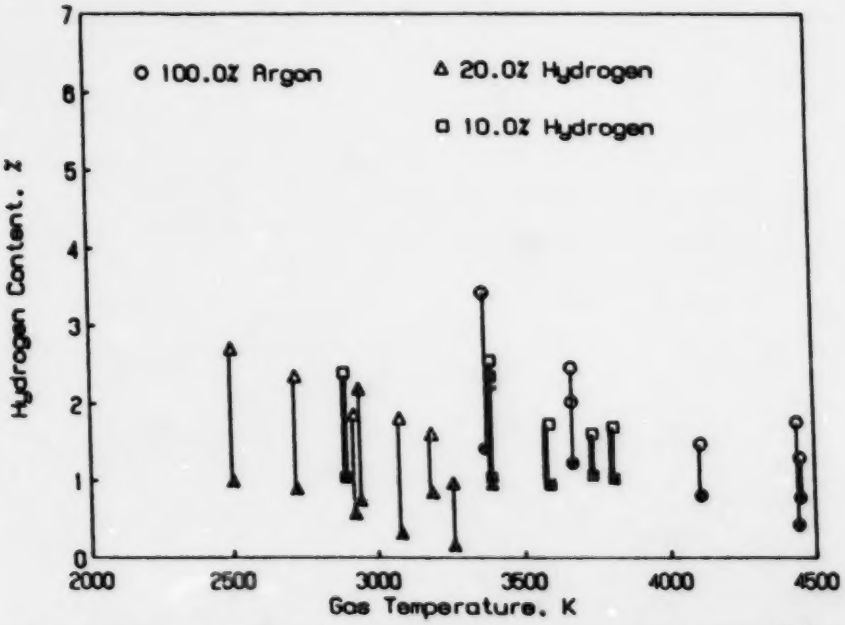

Figure 8: Ratio of Total Hydrogen in Acetylene, Ethylene and Methane to Hydrogen Initially Present in the CANMET Residue (Argon Flow = 20.81 g/min Radial and 37.22 g/min Swirl, Hydrogen Flow = 0.32 or 0.73 g/min to the Tailflame)

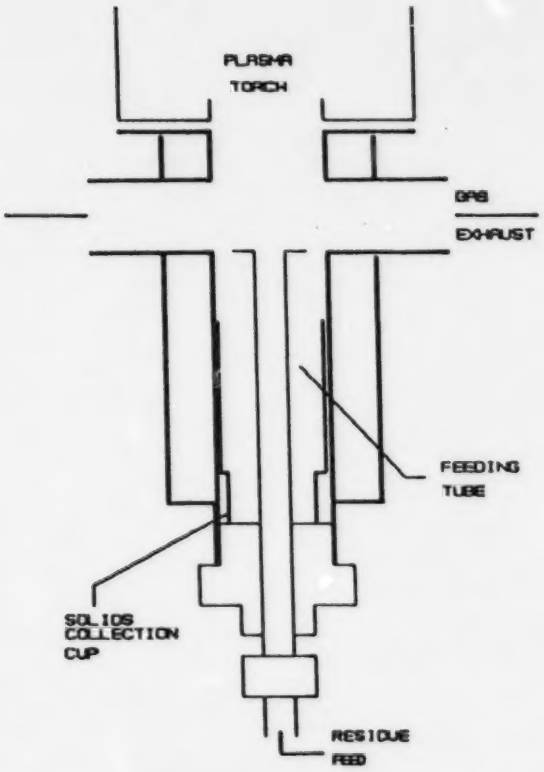

Figure 9: Continuous Reactor

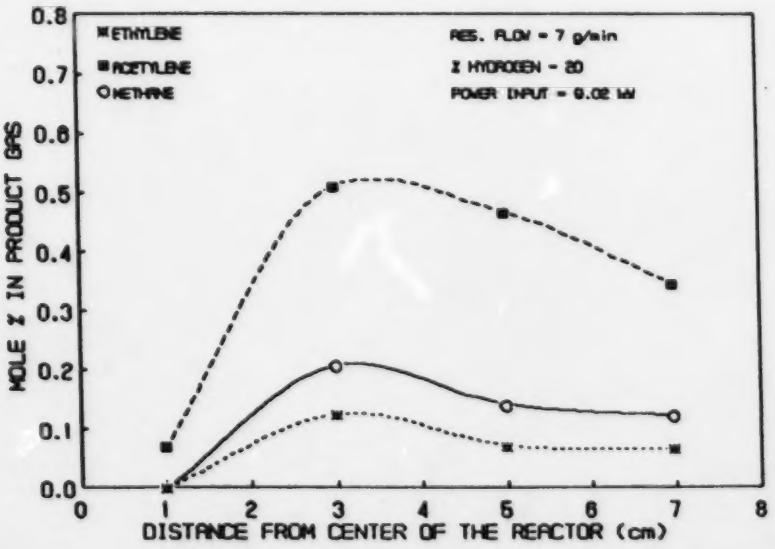

Figure 10: Effect of Sampling Probe Position on Product Concentration

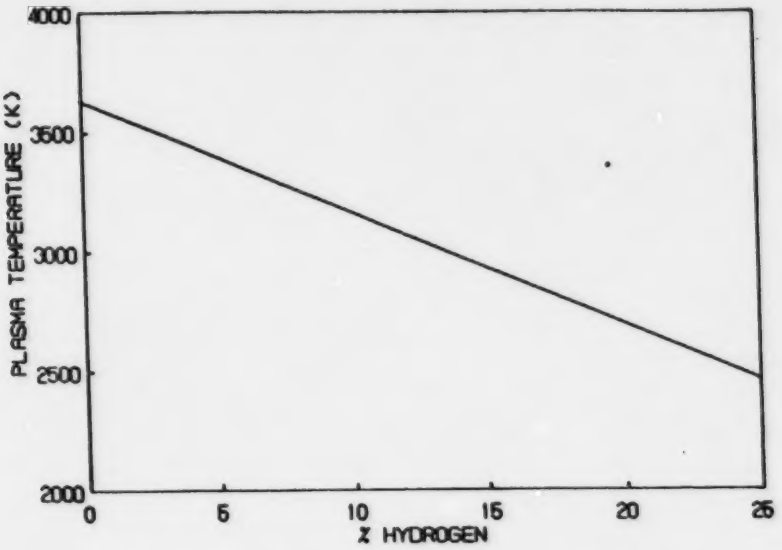

Figure 11: Plasma Temperature at Constant Power (9.02 kW) as a Function of Hydrogen Concentration

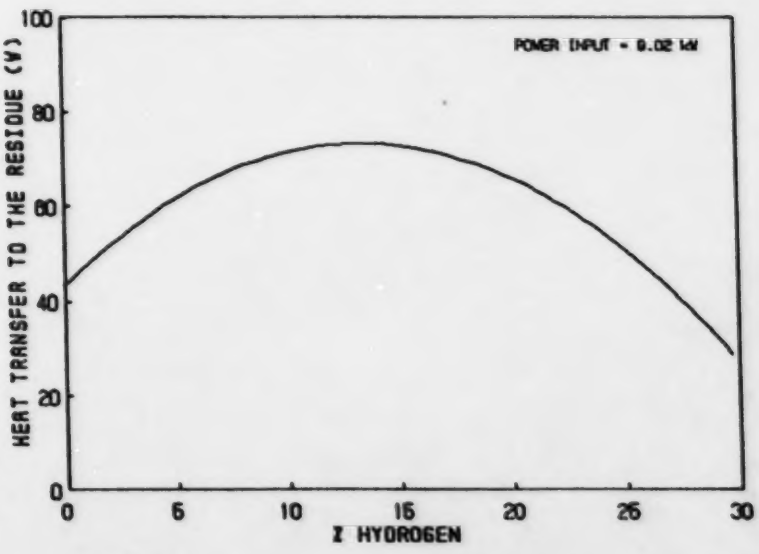

Figure 12: Predicted Heat Transfer to Residue at Constant Power (9.02 kW) as a Function of Plasma Hydrogen Concentration

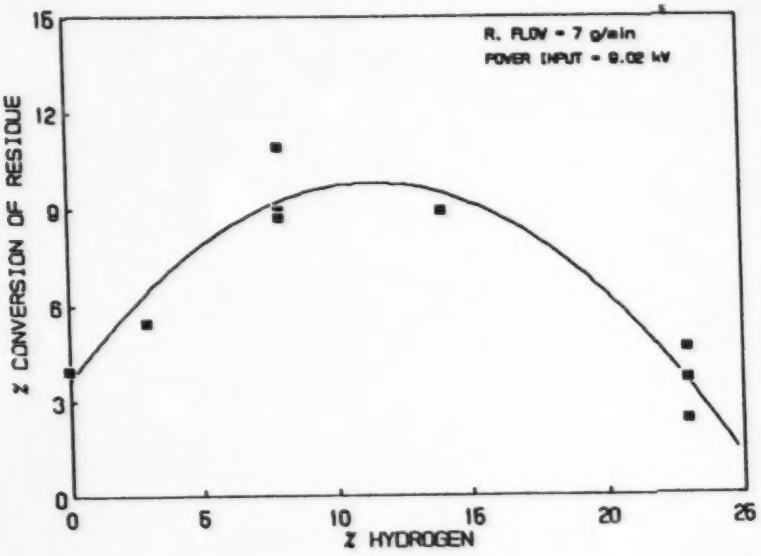

Figure 13: Conversion of Residue as a Function of Plasma Hydrogen Concentration

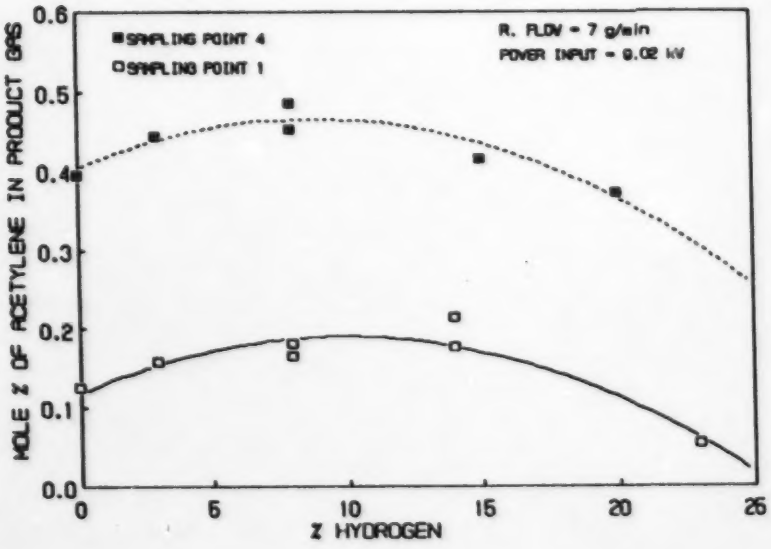

Figure 14: Concentration of Acetylene as a Function of Plasma Hydrogen Concentration

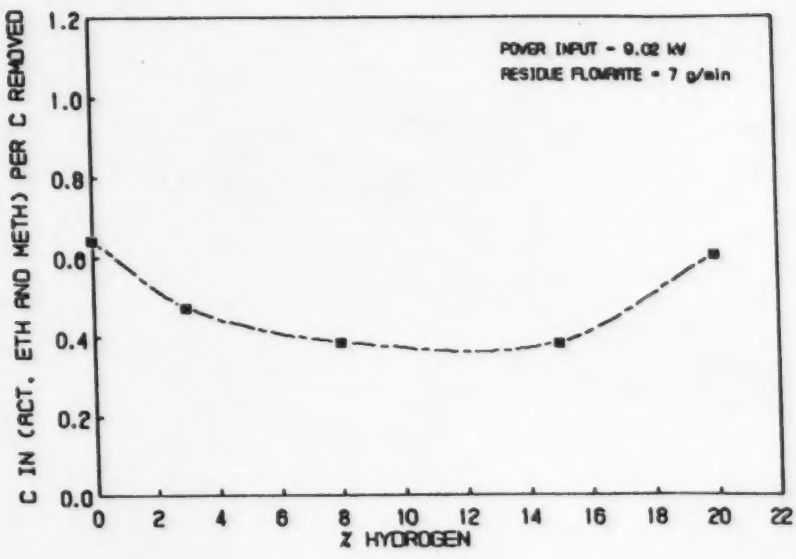

Figure 15: Yield of Gaseous Hydrocarbons as a Function of Plasma Hydrogen Concentration

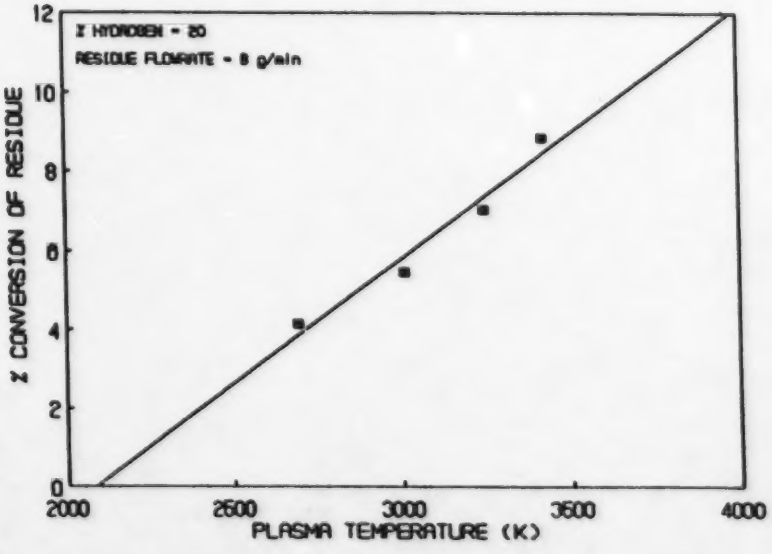

Figure 16: Conversion of Residue as a Function of Plasma Gas Temperature at Constant Flow Rate

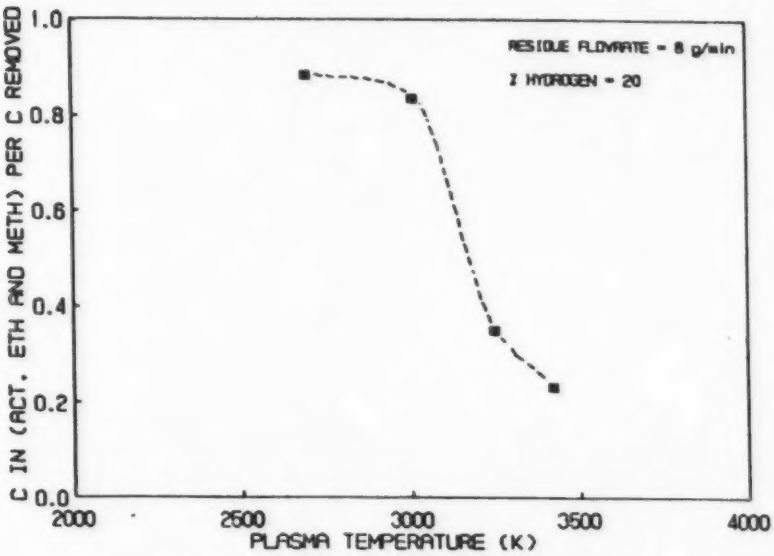

Figure 17: Yield of Gaseous Hydrocarbons as a Function of Plasma Gas Temperature at Constant Residue Flow Rate

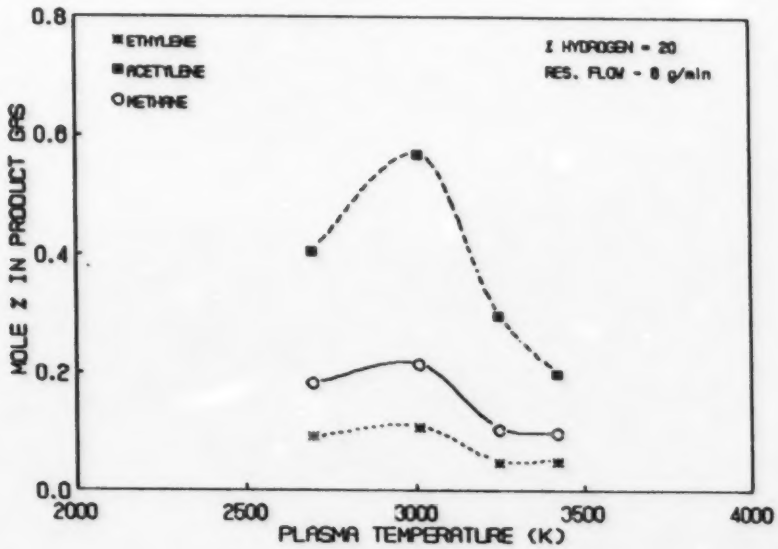

Figure 18: Concentration of Hydrocarbons in Product Gas as a Function of Plasma Gas Temperature at Constant Residue Flow Rate

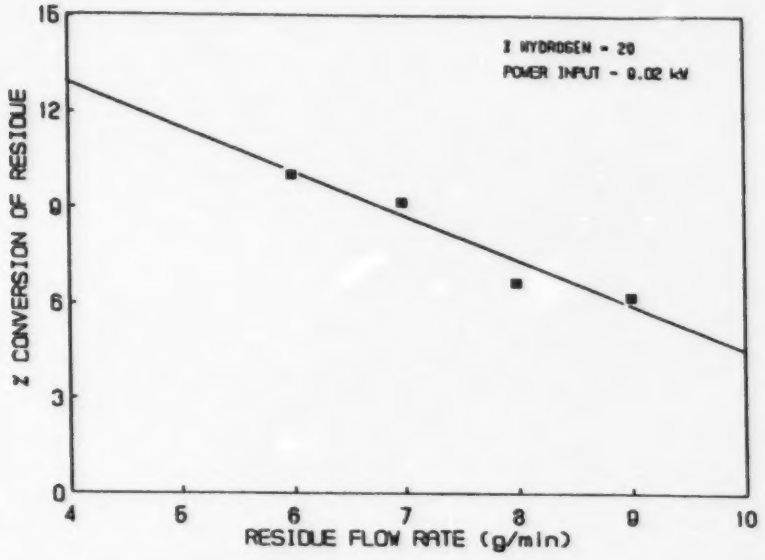

Figure 19: Conversion of Residue as a Function of Residue Flow Rate

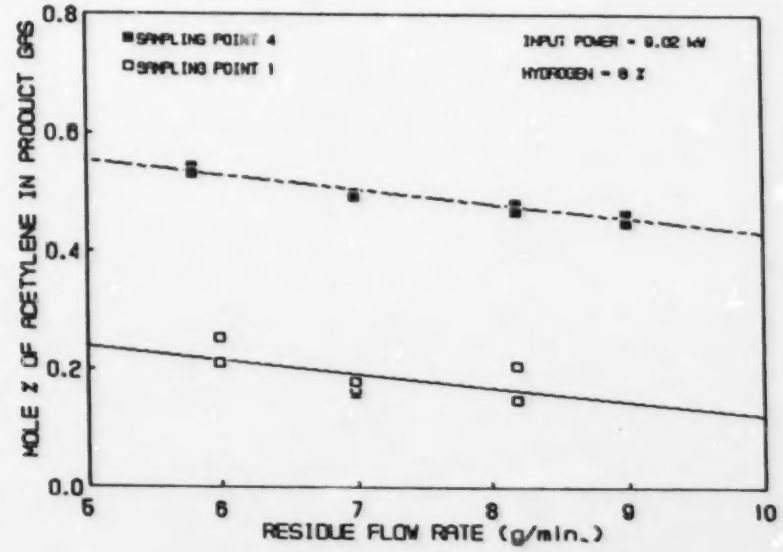

Figure 20: Concentration of Acetylene in Product Gas as a Function of Residue Flow Rate